12 CALCIUM AND MAGNESIUM

Calcium and magnesium, two secondary plant nutrients, have several common characteristics. Some of these are as follows:

1. Both have only one active valence 2^+.
2. Both are taken up by plants as cations.
3. Both are basic or base-forming elements.
4. They occur together in nature as dolomitic limestone.

However, they differ in regard to their presence and functions in plants. Calcium is present in the cell wall, is involved in cell division, and is therefore an important component of plant structure; it is generally considered an immobile element in plants. Calcium in soils serves as an excluder or detoxifier of heavy metals such as Ni, as well as other elements that might otherwise be toxic. In addition, Ca provides protection against drought, salinity, and mechanical stress (Foy, 1992). Magnesium, on the other hand, is the core cation in the structure of the chlorophyll molecule and is thus vital to photosynthesis. Magnesium also serves as a structural component in ribosome and thus plays an important role in protein synthesis. It is fairly mobile in plants.

12.1. CALCIUM AND MAGNESIUM IN SOIL

Calcium is present in the earth's crust in much larger amounts (3.64%) than magnesium (1.93%). Highly weathered, coarse, sandy soils in humid regions may contain 0.1% total Mg and 0.1 to 0.3% total Ca, while fine-textured, clay soils rich in 2:1 layer silicates may contain 0.7 to 3% total Ca and often equal quantities of Mg. Values greater than 3% total Ca in soils indicate the presence of calcium carbonate. Such soils are known as calcareous soils, which may contain less than 1 to more than 25% total Ca. These soils may have a hard pan of calcium carbonate and calcium silicate at a rather shallow depth in soil profile. In soils developed from calcareous glacial tills, Ca is usually leached to the depth of rooting where it precipitates as calcium carbonate. Also, some temperate soils subjected to temporary flooding may contain small, calcareous, mollusk shells on or near the soil surface.

Calcium in soils is derived from the minerals anorthrite, pyroxenes (augite), amphiboles (hornblende), and albite. Calcite ($CaCO_3$) is the most important source of Ca in calcareous soils; when present, dolomite ($CaMg [CO_3]_2$) also contributes to soil Ca. In arid and semiarid regions gypsum ($CaSO_4$ $2H_2O$) could be an important source of Ca.

Magnesium in soils is derived from minerals biotite, phologpite, hornblende, olivine, and serpentine. In calcareous soils dolomite, when present, is an important source of soil Mg. In arid and semiarid regions substantial amounts of mineral epsomite ($MgSO_4$ $7H_2O$) may be present and may contribute to soil Mg.

Both Ca and Mg are present in nonexchangeable and exchangeable forms and in soil solution; the latter two forms remain in a dynamic equilibrium. The degree of calcium saturation of exchange complex required for optimum plant growth varies from crop to crop, and often wide variations exist between different cultivars of a species. Thus the optimum range of Ca saturation of the exchange complex (CEC) is wide (12 to 75%); for temperate regions and for a number of crops the suggested optimum is 65% (Eckert and McLean, 1981). On the other hand, the range for critical Mg saturation levels is narrow, often 5 to 10% of CEC.

Exchangeable Ca in soils can range from <25 mg kg^{-1} to more than 5000 mg kg^{-1}. Ca in soil solution may range from 68 to 778 mg kg^{-1}. Exchangeable Mg generally constitutes 4 to 20% of the CEC, and the concentration in soil solution may range from 50 to 120 mg L^{-1}.

When solution Ca or Mg is depleted by leaching or plant uptake, more Ca or Mg is released from the solid phase.

12.2. FACTORS AFFECTING THE AVAILABILITY OF CALCIUM AND MAGNESIUM IN SOILS

Release of Ca^{2+} or Mg^{2+} from the exchange complex and their availability to crop plants depends upon the following factors; a number of these are interdependent:

1. Total Ca or Mg supply
2. Type of clay minerals present
3. Cation exchange capacity (CEC) of soil
4. Percentage saturation of CEC with Ca^{2+} or Mg^{2+}
5. Soil pH
6. Ratio of Ca^{2+} or Mg^{2+} to other cations in soil solution

Soils having 2:1 layer silicates have higher CEC and can thus retain larger amounts of Ca or Mg. In such acid soils, however, Ca level may be too low to be available to plants. Smectites require nearly 75% saturation of exchange complex before appreciable Ca^{2+} is released for plant uptake. On the other

hand, soils having 1:1 layer silicates (kaolinites) will release exchangeable Ca into the soil solution at only 20 to 40% Ca saturation of the exchange complex.

Soil pH is inversely related to exchangeable Ca. In acid soils, which can have high exchangeable Al, Ca concentrations become low. Liming such soils increases soil pH by increasing saturation of exchange complex with Ca^{2+}, which replaces exchangeable H^+. Absolute Ca deficiency and Ca deficiency symptoms are rarely seen in the field. Even in cases where the deficiency symptoms are observed, they are more likely due to Al-Ca antagonism than to low Ca supply *per se* (Foy, 1992). For example, in a study with barley cultivars, Al-sensitive Kearney barley developed Ca-deficiency symptoms (rolling and eventual collapse of youngest leaves) (Figure 12.1), but Al-tolerant Dayton did not show Ca-deficiency symptoms (Long and Foy, 1970). Al also antagonizes Mg uptake, and there are reports indicating Al-toxicity is a factor in controlling the severity of Mg deficiency (Grimme, 1984). Nevertheless, critical experimentation using $CaSO_4$ as a source of Ca, $MgCO_3$, or MgO for correcting exchangeable Al and $Ca(OH)_2$ for correcting both exchangeable Al and Ca deficiency has illustrated that Ca deficiency could be a limiting factor for plant growth on some acid ultisols (Adam and Moore, 1983; Njohn et al., 1987). Also, in acidic, sandy soils (primarily quartz sands) Ca deficiencies may be expressed.

Availability of Ca^{2+} and Mg^{2+} and their uptake by plants is largely influenced by the ratio of these cations with other cations. A Ca:(Ca+Mg+K) ratio in solution of 0.1 to 0.2 is generally considered desirable for adequate Ca uptake. Excess Ca may adversely affect Mg uptake, and a Ca:Mg ratio in solution greater than 7:1 is not considered desirable (Tisdale et al., 1985). This would explain why continuous liming of coarse-textured soils may lead to Mg deficiency (due to an increased Ca:Mg ratio). On the other hand, Ca:Mg ratios less than about 2:1 can result in high exchangeable Mg restricting adequate Ca uptake, causing Ca-deficiency symptoms in soils developed from some marine shales. Similarly, K^+ antagonizes Mg uptake (Figure 12.2), and this could be a concern in low-Mg soils. The recommended K:Mg ratios are <5:1 for field crops; 3:1 for vegetables and sugar beets, and 2:1 for fruits and greenhouse crops (Tisdale et al., 1985).

12.3. LEACHING OF CALCIUM AND MAGNESIUM

Calcium is often the dominant cation in drainage waters, springs, streams, ponds, and lakes. The annual leaching loss of Ca and Mg from a soil will depend on the total amounts present in a soil, its CEC, and the frequency and intensity of precipitation and in irrigated areas on the amount of irrigation water applied and its Ca and Mg content. The provision of a plant canopy such as grass cover can greatly reduce the leaching of Ca and Mg from a soil (Table 12.1). Excessive leaching of Ca is one factor responsible for the development of acidity in oxisols and ultisols. Excessive leaching of Ca and Mg in humid regions is also the reason why Ca- and Mg-responsive soils are mostly present in humid regions of the Appalachian range and in the south coastal

Figure 12.1. Al-induced Ca deficiency in Al-sensitive Kearney barley. No deficiency symptoms were developed in Al-tolerant Dayton barley. (From Long and Foy, 1970. Agron. J. 62:679–681. With permission of ASA.)

United States. In less humid regions, during soil development, some Ca and Mg was leached from the surface soil and precipitated mainly as carbonates and sulfates in the subsoil. This is common in the mollisols of the midwestern United States.

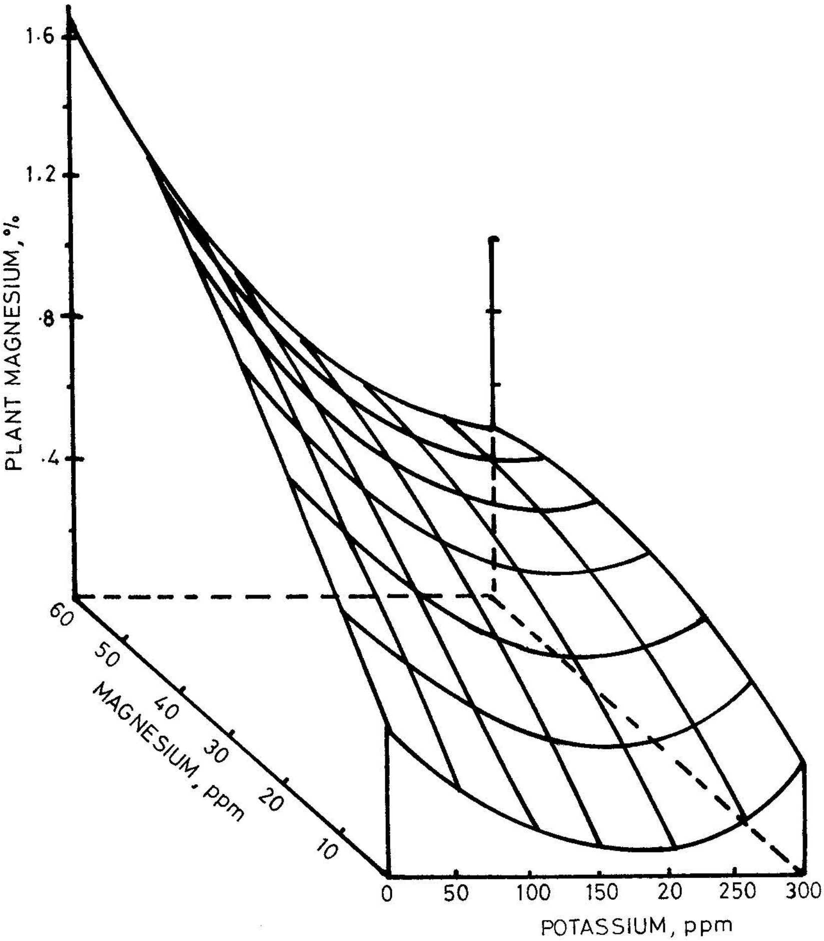

Figure 12.2. Predicted response surface of magnesium concentration in top tissue of sorghum to increasing levels of potassium and magnesium concentrations in nutrient solution at 75 days after seedling emergence. (From Ologunde and Sorensen, 1982. Agron. J. 74:44. With permission of ASA.)

12.4. DETERMINING AVAILABLE CALCIUM AND MAGNESIUM

The most common extractant for determining exchangeable (available) Ca and Mg is molar ammonium acetate at pH 7.0 (Lanyon and Heald, 1982). Exchangeable Ca levels, at which crops are no longer expected to respond to Ca application, vary considerably and range from 250 mg kg^{-1} in sandy soils to 500 mg kg^{-1} in silty clay soils. Several researchers prefer the Ca^{2+} saturation

Table 12.1 Estimated Annual Ca and Mg Drainage Losses from a Sandy, Loam Soil in Orchard Lysimeters at Summerland, B.C.

Vegetation	1978	1979	1980
Calcium (kg ha^{-1} yr^{-1})			
Grass[a] cover	259	117	367
No grass	1045	275	578
Magnesium (kg ha^{-1} yr^{-1})			
Grass cover	82	35	136
No grass	293	71	194
Precipitation and irrigation (mm)			
Precipitation	330	240	320
Irrigation[b]	670	690	860

[a] Kentucky bluegrass (*Poa pratensis*).

[b] Irrigation water generally contained 28×10^{-6} kg Ca L^{-1}, and 9×10^{-6} kg Mg L^{-1}.

Adapted from Nielsen and Stevenson (1983).

percentage of CEC as the criterion for determining Ca availability in soils (this has already been discussed). For determining Ca needs of peanut or groundnut (*Araclis hypogaea* L.) the soil is generally extracted with Mehlich I (0.05 mol L^{-1} HCl + 0.0125 mol L^{-1} H_2SO_4) (Mehlich, 1953). A value of 290 kg Ca ha^{-1} is considered the upper limit at which a response to Ca application can be expected. A Cate-Nelson (1971) graph relating peanut yield and log Mehlich Ca is shown in Figure 12.3.

Similarly, the exchangeable Mg level recommended for agronomic crop production ranges from 25 to 180 mg kg^{-1} soil. Again, several researchers prefer the Mg^{2+} saturation percentage of CEC as the criterion for determining available Mg. For example, response of cotton to Mg application on heavy, clay soils was found to be excellent at 3% Mg^{2+} saturation of soil CEC, and no response was obtained at 6.4% saturation (Lancaster, 1958). The general consensus is that 5% Mg^{2+} saturation of CEC of soil is needed for most crops other than alfalfa, corn silage, and cool season forage crops, which need higher Mg^{2+} saturation (10% of CEC) to avoid grass tetany in ruminant animals. Grass tetany is a disorder of ruminants caused by Mg concentrations less than 2 g kg^{-1} forage (dry-matter basis). The factors responsible for this include K concentration >30 g kg^{-1}, K/(Ca+Mg) equivalent ratio >2.2 and N concentration >40 g kg^{-1} in the plant (dry matter basis) (Grunes and Mayland, 1975).

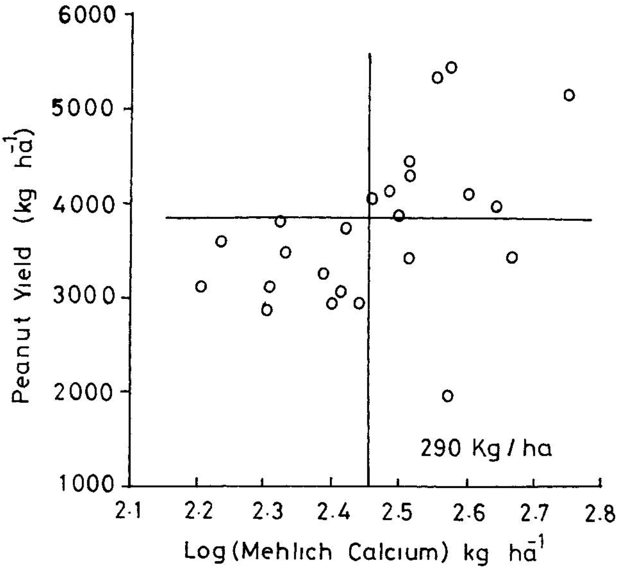

Figure 12.3. Relationship between pod yield and Log of Mehlich I Ca in Lakeland sand 90 days after planting. The vertical and horizontal coordinates show the partitioning of the data points according to the Cate-Nelson technique. The point of intersection of the vertical coordinate with the x-axis represents Ca level beyond which yield response is very minimal. (From Alva et al., 1989. Commun. Soil Sci. Plant Anal. 20:1742. With permission of Marcel Dekker, Inc.)

12.5. CALCIUM AND MAGNESIUM DEFICIENCY SYMPTOMS

Since Ca is generally immobile in plants, there is very little translocation of Ca in phloem. This leads to a poor supply, and consequent deficiency symptoms often result in storage organs and fruits. Bitter pit development in apples is a good example of this. Blossom-end rot in tomatoes and moldy, diseased, and low quality soybeans are some other examples. Terminal buds and apical tips of roots in plants fail to develop. Acute Ca deficiency in corn prevents the emergence and unfolding of young leaves, the tips of which may be covered with a sticky gelatinous material (Figure 12.4); the leaves tend to stick together giving a ladder-like appearance.

As a contrast to Ca, Mg is fairly mobile in plants and its deficiency symptoms appear first on the lower leaves. In corn, Mg deficiency results in interveinal chlorosis of the lower leaves (Figure 12.5); only the veins remain green. In cotton the lower leaves develop a reddish purple cast that may gradually turn brown and necrotic.

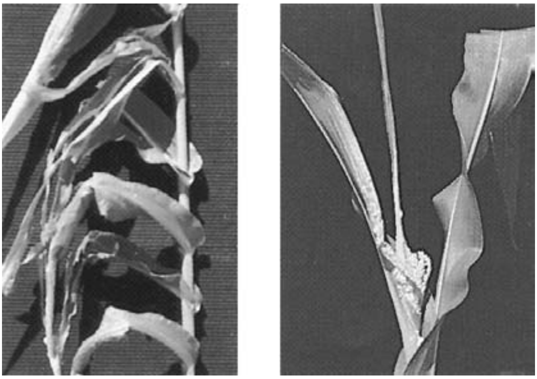

Figure 12.4. Calcium deficiency. The leaf tips stick to the next lower leaf, giving a ladderlike appearance (left). The young leaves of new plants are affected first. They are often distorted and small, the margins are irregular in form, and the leaves frequently show spotted necrotic areas. There may be dieback of the growing tip (right). Root growth is markedly impaired. (From *Corn Field Manual*, J.R. Simplot Company Minerals & Chemical Division, Pocatello, ID, ©1984. With permission.) See Plate 3 following p. 170.

12.6. CALCIUM AND MAGNESIUM AMENDMENTS

Most Ca and Mg amendments are applied as liming materials on acidic soils, and these have already been discussed in Chapter 5. In addition to liming materials, gypsum ($CaSO_4$), because it has higher water solubility than limestone, has received special attention for supplying Ca to peanut or groundnut. Calcium absorbed by the roots is not translocated to the developing pods, which therefore absorb directly from the soil solution the Ca needed for their development during initial pegging and seed development. For this purpose gypsum is generally band applied or broadcast during the first-bloom stage; the term lime plastering is sometimes used for this practice. The release of Ca^{2+} from gypsum is influenced by the particle size, so finely powdered material is generally used. Data from a field experiment conducted on Lakeland sand in Georgia (Alva et al., 1989) are presented in Table 12.2. Gypsum application increased the pod yield, as well as the percentage of sound, matured kernels (SMK); crystalline and fine powder (wet) were better than other materials.

Dolomite is the most widely used Mg amendment. The other commonly used material is Epsom salt ($MgSO_4$), which can be also used in foliar sprays when a Mg deficiency is detected at a later crop growth stage. Mg deficiency in citrus orchards in California is frequently corrected by foliar spray of $Mg(NO_3)_2$. Mg-chelates are also marketed and used.

Figure 12.5. Magnesium deficiency. Interveinal chlorosis starts on the lower leaves (top). Yellow streaking sometimes changes to dead, round spots, which gives the impression of beaded streaking (below). The older leaves may become reddish purple on the tips, edges, and underside and die in extreme cases. (From *Corn Field Manual*, J.R. Simplot Company Minerals & Chemical Division, Pocatello, ID, ©1984. With permission.) See Plate 4 following p. 170.

Table 12.2 Effect of Various Gypsum Amendments on Pod Yields and Grades in Peanut on Lakeland Soil in Georgia

Gypsum materials	Pod yield[a] (Mg ha^{-1})	SMK[b] (%)
Crystalline	4.48 a[c]	70 a
Fine powder (wet)	4.38 ab	69 a
Coarse powder	4.11 abc	68 a
Fine powder (dry)	3.86 abc	68 a
Granular 1	3.46 abc	70 a
Granular 2	3.30 bc	68 a
Pelleted	3.10 c	67 a
Control (no gypsum)	3.03 c	61 b

[a] Adjusted to 7% moisture.

[b] Sound, mature kernels.

[c] The means followed by same letter are not significantly different at p = 0.10.

Adapted from Alva et al. (1989).

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